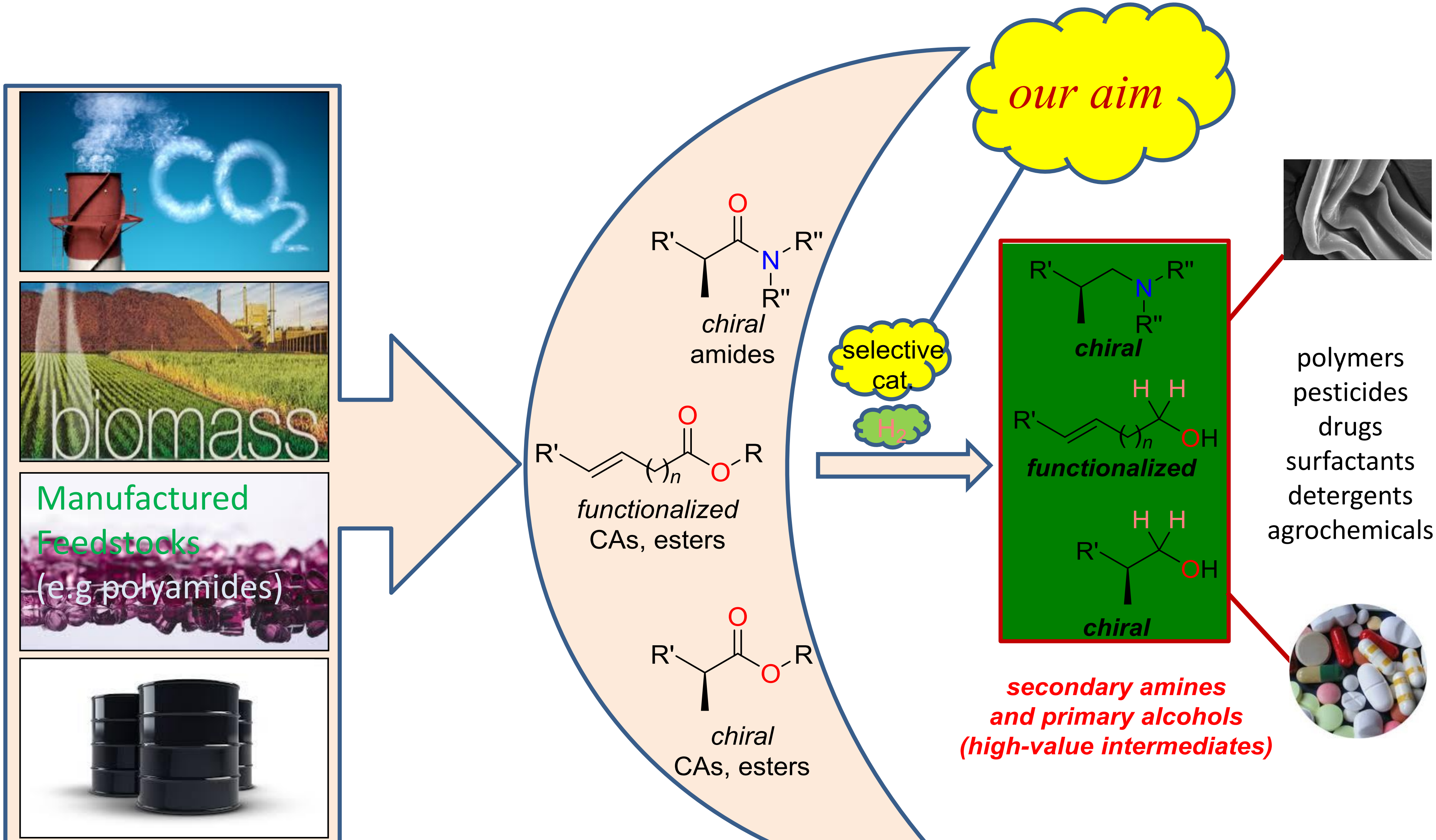
Introduction

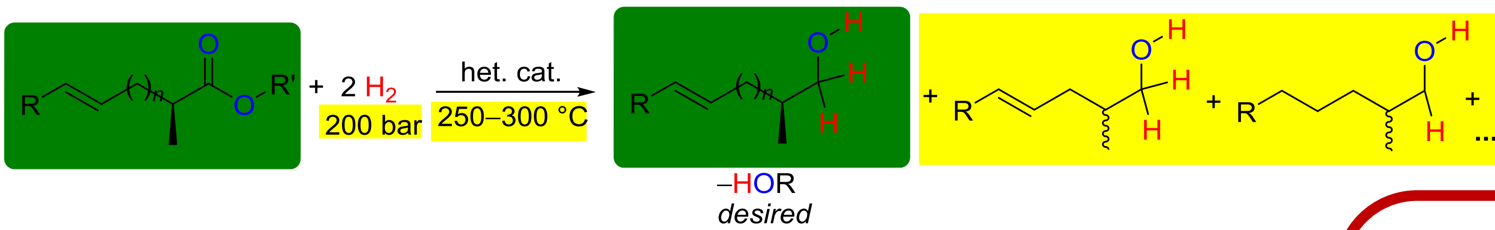
- DOE: 25% of petro-derived chemicals to be replaced with bio-renewable ones by 2025
- Many of Platform Chemicals Contain Carbon–Oxygen Bonds
- Our Aim: Next Generation of Efficient Molecular, Enzymatic or Chimera-Based Catalysts

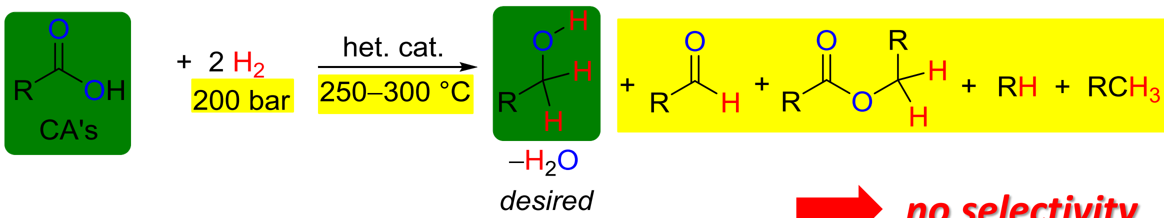


http://www.lanl.gov/expertise/profiles/view/pavel-dub

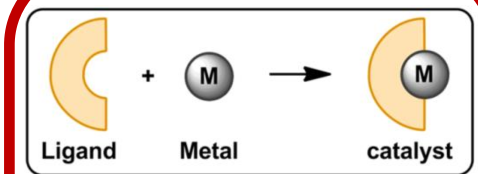
Introduction: why in particular molecular catalyst?

problems of traditional approach:





no selectivity

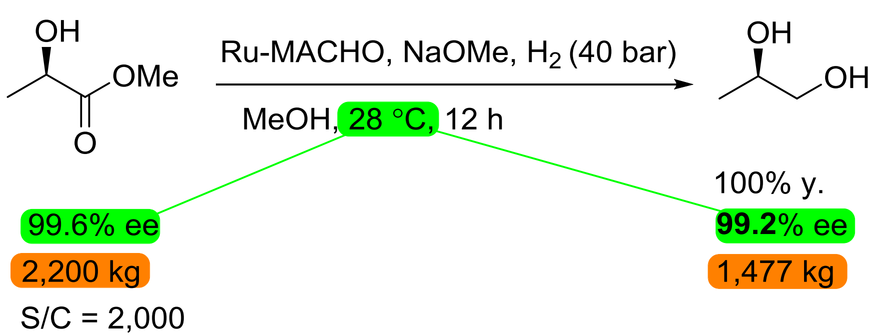


- –Mild reaction conditions
- –High activity & selectivity
- –Atom economy
- –Cost efficieny
- –Operational simplicity

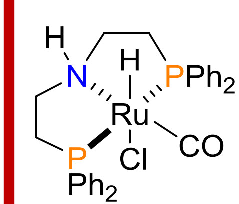
exemplary reaction:

multiton-scale
(*R*)-1,2-propanediol synthesis

TAKASAGO



Ru-MACHO:

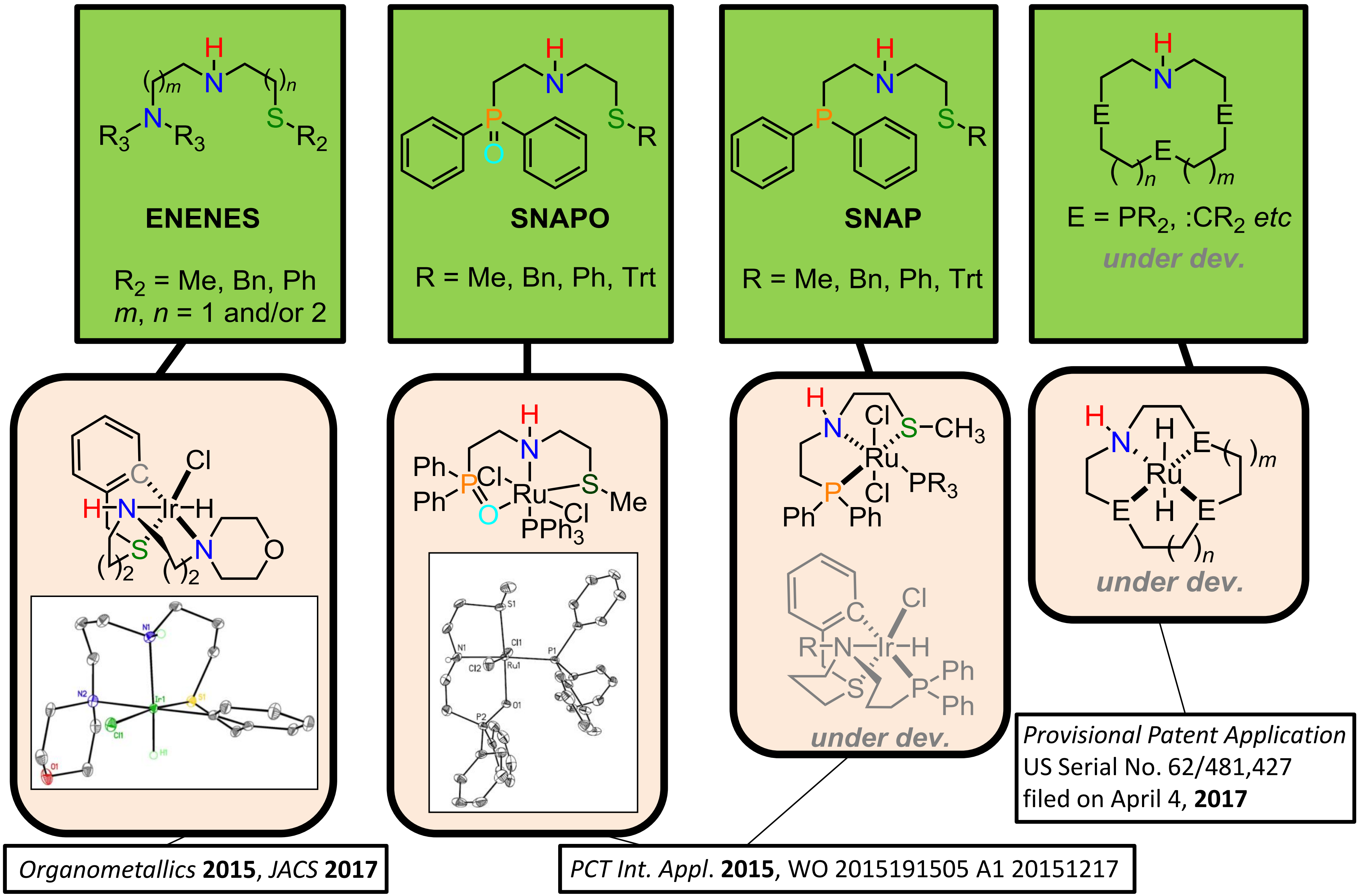


6.4 kg

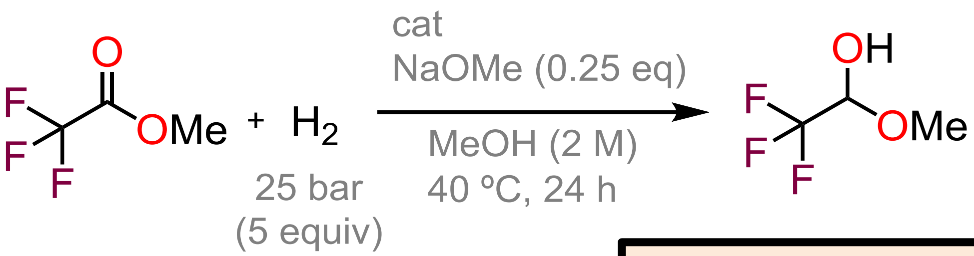
Kuriyama, W; Saito, T. et al *Org. Process Res. Dev.* **2012**, *16*, 166

low temperature is important to prevent racemization

LANL Ligands and Molecular Catalysts for the Chemical Reductions of Carbon–Oxygen Bonds in Renewable and Oil-Based Feedstocks



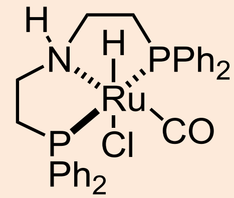
Example 1: Chemoselective Hydrogenation of Fluorinated Esters into Hemiacetals with ENENES-based Ir Catalyst



S/C = 20 000

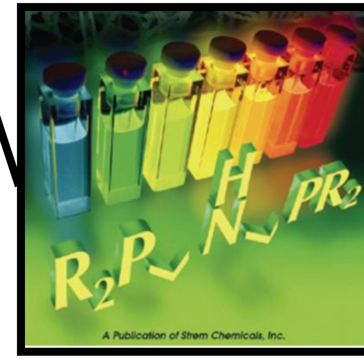
Ru-MACHO catalyst:
yield: 96%
selectivity: 75%

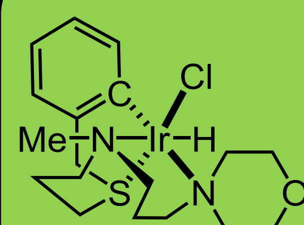
LANL Ir catalyst:
yield: 91%
selectivity: 96%



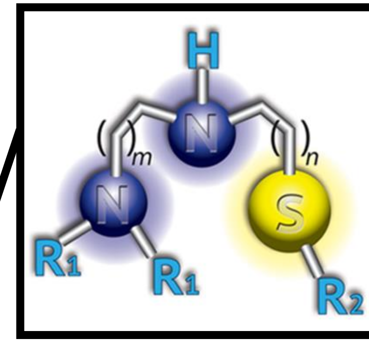
Ru-MACHO
Takasago Int Corp
739103 Aldrich
$200/g

ligand toolbox

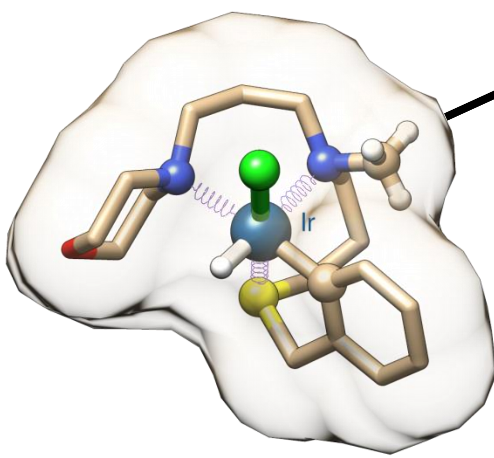




LANL Ir-catalyst

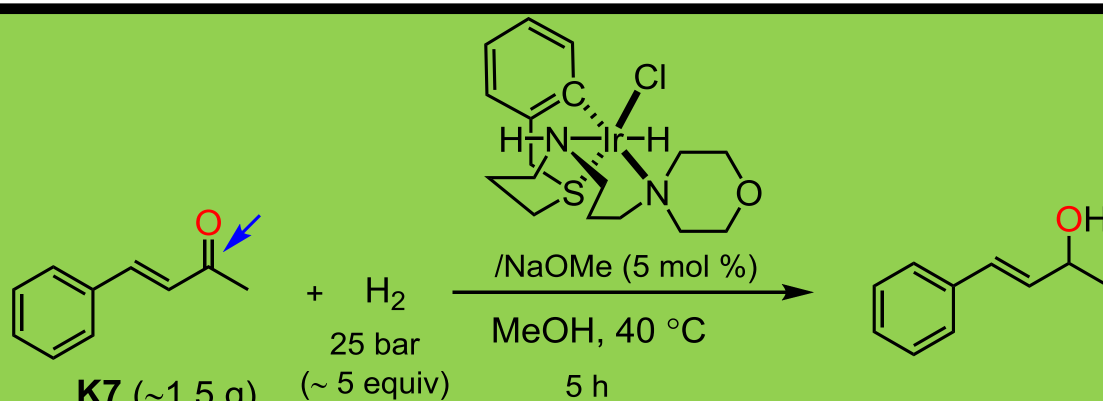


ENENES
(cheap, multi-gram scale, air-stable)



PCT/US2015/034793
Organometallics **2015**, *34*, 4464
JACS **2017**, 139, 1245

Example 2: Chemoselective Hydrogenation of α,β-unsaturated Ketone with ENENES-based Ir Catalyst



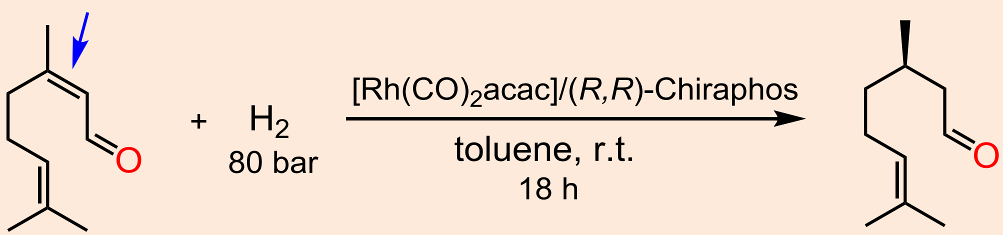
K7 (~1.5 g)

>99% conversion

S/C = 100 000

~94% C=O/C=C selectivity

Dub, P. et al. *JACS* **2017**, *139,* 1245



BASF
The Chemical Company

99.9% conversion

S/C = 1000

99.8% C=C/C=O selectivity

90% ee

Paciello, R. et al. WO2009068444A2

Example 3: Chemoselective Hydrogenation of Bio-Derived Fatty Ester

Givaudan

Geisser, R. W.; Oetiker, J. D.; Schröder, F.
WO2015EP51219 20150122
(priority date Jan 4, 2014)

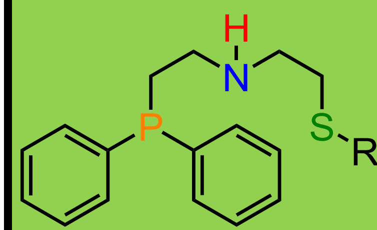
Los Alamos NATIONAL LABORATORY

Dub, P. A.; Gordon, J. C.
WO 2015191505 A1 20151217
(priority date Jun 9, 2014)

TAKASAGO

Nakayama, Y.; Ogata, O.
WO 2016031874 A1
(priority date Aug 26, 2014)

Independently developed

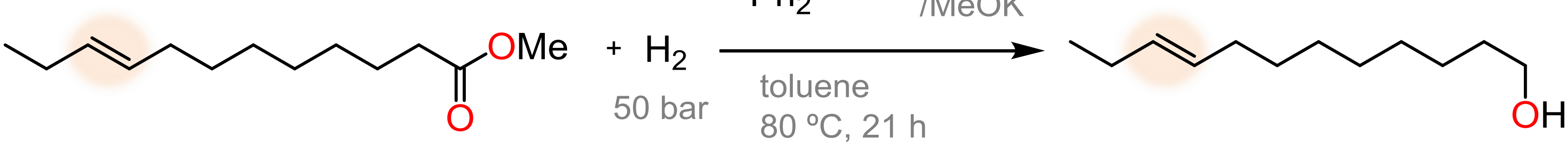
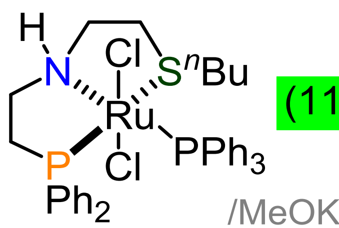


SNAP

R = Me, Bn, Ph, Trt

surfactants
detergents
agrochemicals

natural oil

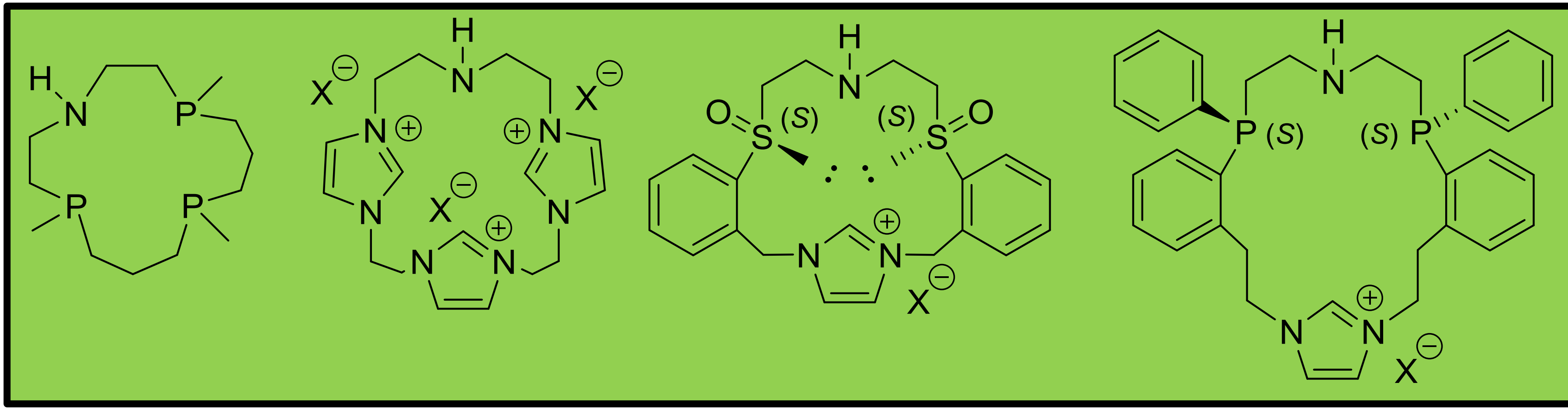
(11 mg)

30 g

S/C = 10 000

21.5 g (83%)
98% purity
E/Z = 85/15
described by Givaudan

Novel Tetradentate Macrocyclic Ligands and Catalysts for the Chemical Reduction of Carbon–Oxygen Bonds in Renewable Feedstocks Including CO_2, Biomass and Manufactured-Derived



Prophetical examples described in Dub, P. A.; Schmidt, J. G.; Gordon, J. C.
Provisional Pat. Appl. US Serial No. 62/481,427 filed on April 4, **2017**

Searching sponsors/collaborators to develop the chemistry and new IP

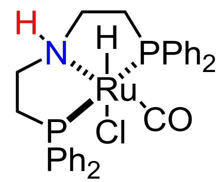
Potential Example 1: CO_2 captured from air into Methanol

$$CO_2 + H_2 \xrightarrow{\text{Ru-MACHO/additives}} CH_3OH$$

TON = up to 2000!!!

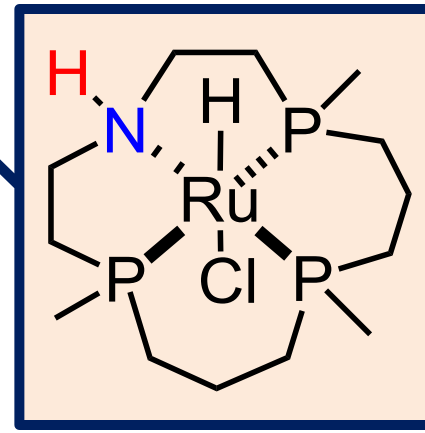
Prakash & Olah, *J. Am. Chem. Soc*. 2016, 138, 778−781

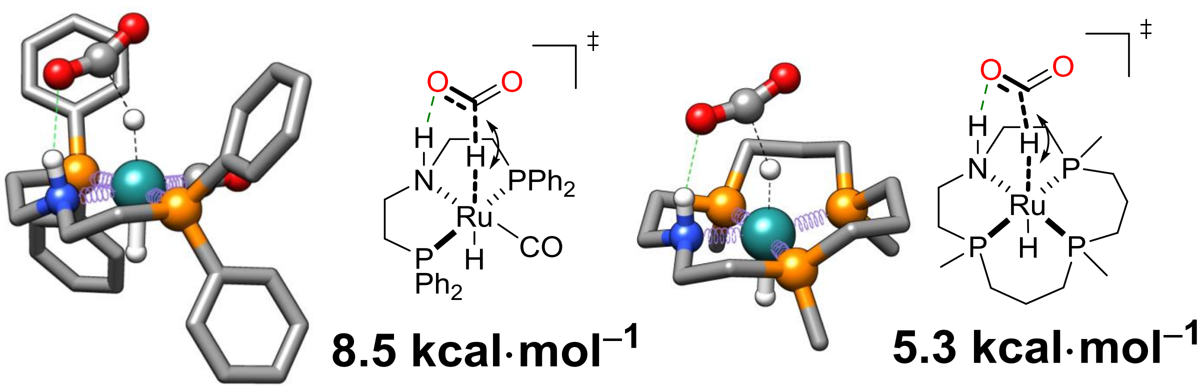
Ru-MACHO:



TAKASAGO

Next Generation of Efficient Catalysts for Fine Chemical Industries





*i*455cm^{-1} *i*210 cm^{-1}

$\Rightarrow$ ***k_1/k = 227***

M06L/SDD(Ru)/6-31G*(all others) level of theory $\Delta G_{298K}^{\circ\neq}$

- ✓ Potential increase of the S/C from 2,000 to 450,000!
- ✓ Greater stability due to macrocyclic nature
- ✓ Ketones, carboxylic and carbonic acid derivatives